Journal of Environmental Chemical Engineering 7 (2019) 103184

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Techno-economic analysis of anaerobic digestion implementation in small Italian breweries and evaluation of biochar and granular activated carbon addition effect on methane yield

Matia Mainardis[a,b,*], Simone Flaibani[a], Fabio Mazzolini[a], Alessandro Peressotti[c], Daniele Goi[a]

[a] Polytechnic Department of Engineering and Architecture (DPIA), Via del Cotonificio 108, 33100, Udine, Italy
[b] CAFC S.p.A., Viale Palmanova 192, 33100, Udine, Italy
[c] Department of Agricultural, Food, Environmental and Animal Sciences (DI4A), Via delle Scienze 206, 33100, Udine, Italy

ARTICLE INFO

Keywords:
Brewery spent grain
Anaerobic digestion
Energy recovery
Biogas
Biochar

ABSTRACT

The aim of the work was to evaluate the techno-economic feasibility of anaerobic digestion implementation in small breweries located in the mountain area of Friuli-Venezia Giulia region (Italy). A territory-oriented approach was adopted, analysing the production of organic residues in local breweries and the potential methane production from each residue. An energy balance and a simplified dimensioning for anaerobic reactor installation at brewery scale was proposed, analysing actual energy consumption and the effect of biogas on plant energy balance improvement. Brewery spent grain, spent yeast, whirlpool residue and end-of-fermentation beer were identified as the main organic residues in the analysed plants. Biochemical methane potential tests revealed high methane potential of spent yeast, up to 486.9 NL CH_4/kg VS_{added}, and spent grain, up to 356.2 NL CH_4/kg VS_{added}. Granular activated carbon and biochar were added to selected tests to evaluate an eventual increase in methane yield; a noticeable effect was observed in particular on spent yeast, due to the enhanced microorganism activity and C/N ratio optimization. Co-digestion tests were performed on spent grain and spent yeast: a synergistic effect arose with a mixture of 70% spent yeast and 30% spent grain, where methane yield increased up to 447.7 NL CH_4/kg VS_{added}. Electricity consumption was estimated as 130.6–148.9 MJ/hL, while heat need was 116.4–147.0 MJ/hL; it was showed that anaerobic digestion implementation, through a digester having 65 m^3 volume, could provide up to 53.9% of electric and 64.4% of thermal need of the facility.

1. Introduction

The brewing sector holds a strategic position in the food industry [1]; European Union beer production was as high as 383,553,000 h L and Italian beer production was 13,256,000 h L in 2013 [2]. Brewing organic residues include end-of-fermentation beer, brewery spent yeast (BSY) and spent grain (BSG), as well as whirlpool residue, that comes from hop and trub separation from wort. Biogas production from brewery waste through anaerobic digestion (AD) can help to reduce energy and disposal costs, decreasing carbon footprint [3], by exploiting the high methane potential of organic residues, reducing at the same time the amount of solid material to dispose. Brewery wastewater has been extensively valorised using Up-flow Anaerobic Sludge Blanket (UASB) technology [4]. Spent yeast AD was already investigated [5] and applied also in full scale plants [6].

AD of a single substrate can lead to inhibitory effects, due to a lack of alkalinity or an ammonia excess. In these cases, it appears advantageous to adopt co-digestion processes, that consist in an instantaneous digestion of two or more substrates [7]. The primary concern of co-digestion is to increase methane generation, but it also helps to achieve process stabilisation, favour nutrient balance and obtain synergistic effects for microorganisms, reducing green-house gases emissions and processing costs [8].

BSY is rich in organic solids and can be used as an additional substrate in a UASB reactor to produce more biogas and save the natural gas used in the brewing process [5]. BSY can deliver a high biogas yield of 0.45-0.72 m^3/kg VS (Volatile Solids), even if it is characterized by a high nitrogen content (11–13 g/L) [9]. BSG was historically used as food supplement and cattle feed [1], but in recent years it was considered as an energy substrate. BSG worldwide production was estimated as 38.6×10^6 tons [10], so there is an economic interest to produce renewable energy from this substrate [11]. BSG provides a

* Corresponding author at: Polytechnic Department of Engineering and Architecture (DPIA), Via del Cotonificio 108, 33100, Udine, Italy.
E-mail addresses: mainardis.matia@spes.uniud.it (M. Mainardis), flaibani.simone@spes.uniud.it (S. Flaibani), mazzolini.fabio@spes.uniud.it (F. Mazzolini), alessandro.peressotti@uniud.it (A. Peressotti), daniele.goi@uniud.it (D. Goi).

https://doi.org/10.1016/j.jece.2019.103184
Received 29 March 2019; Received in revised form 22 May 2019; Accepted 26 May 2019
Available online 28 May 2019
2213-3437/

Nomenclature

Abbreviations

AD	Anaerobic digestion
BC	Biochar
BMP	Biochemical methane potential
BSG	Brewery spent grain
BSY	Brewery spent yeast
C/N	Carbon to nitrogen ratio
CHP	Combined heat and power
COD	Chemical Oxygen Demand
EE	Electric energy
GAC	Granular activated carbon
H/C	Hydrogen to carbon ratio
I/S	Inoculum to substrate ratio
NL	Normal litres (for gases: 101,325 Pa and 0 °C)
O/C	Oxygen to carbon ratio
TE	Thermal energy
TN	Total Nitrogen
TP	Total Phosphorous
TS	Total Solids
UASB	Up-flow Anaerobic Sludge Blanket
VS	Volatile Solids

Symbols

C_{pwaste}	Specific heat of brewery waste [MJ/t K]
EE_{CHP}	Electric energy produced by CHP unit [kWh/year]
EE_{net}	Net electric energy from biogas plant [kWh/year]
EE_{pump}	Electric energy for pumping [kWh/year]
EE_{pur}	Electric energy for biogas purification [kWh/year]
f	Mixer utilization factor [−]
G	Mixing intensity [s^{-1}]
G_0	Total CH_4 potential of the substrate [mL/g VS]
G(t)	Cumulative CH_4 yield at time t [mL/g VS]
h	Working hours of mixer [h/year]
k	Hydrolysis constant [d^{-1}]
K	Heat flow coefficient [W/h m^{-2} K^{-1}]
λ	Lag phase duration [d]
μ	Dynamic viscosity [Pa s]
m_{waste}	Daily mass of brewery waste [t/d]
P_{mix}	Mixer power [kW]
R_{max}	Maximum methane production rate [mL/g VS d]
SE_{pump}	Specific pump electricity consumption [kWh/m^3]
t	Time [d]
T_{dig}	Digester temperature [K]
T_{waste}	Initial waste temperature [K]
TE_{CHP}	Thermal energy produced by CHP unit [kWh/year]
TE_{disp}	Heat dispersion through digester walls [kWh/year]
TE_{heat}	Thermal energy spent for heating [kWh/year]
TE_{net}	Net thermal energy from biogas plant [kWh/year]
V_{dig}	Digester volume [m^3]
V_{waste}	Brewery waste volume [m^3/year]

substrate for on-site AD, combustion or biochar (BC) formation, promoting energy self-sufficiency [12].

Biochemical methane potential (BMP) tests were used to establish methane production potential of several substrates. BMP procedure involves adding small amounts of selected substrate and inoculum into serum bottles, creating anaerobic conditions and measuring gas production over time; a cumulative gas production curve is obtained and BMP value is expressed as function of added VS (mL CH_4/g VS) [13]. Determining BMP through regression models is a new methodology initiated within the last decade [14]. Like the phase of bacterial growth, biogas production shows a rising curve and a decreasing curve, indicated by exponential and linear equations [15]. Modified Gompertz equation and first-order kinetic model have been applied to simulate AD process in a simple manner [16].

Biochar is a carbonaceous material formed under combustion of plant materials in low-zero oxygen conditions; BC has been tested to improve soil ecosystem, digestate quality and AD process [17]. BC can improve AD process by increasing microbial colonisation surface area, stabilising the buffering, providing nutrients and counteracting substrate-induced inhibition [7]. Furthermore, BC possesses the ability to catalyse AD process by mitigation of ammonia inhibition, support of archaeal growth and methanization of the labile carbon fraction [18]. Granular activated carbon (GAC) is an inexpensive material frequently used as bio-carrer or adsorbent in wastewater treatment and has demonstrated its applicability in facilitating interspecies electron transfer, increasing biological connections between bacteria in AD [19]. There is a strong interest in using BC and GAC in AD, to both increase process recovery rate during substrate-induced inhibition and decrease the nutrient loss before and after land application [20]. System integration of biogas and biochar promises several synergies [18].

Increasing attention has been put on small-to-medium enterprises energy efficiency [21]: it was highlighted that, though energy consumption per company is usually small, globally they constitute an important share of national energy consumption, that in Italy is as high as 60% [22]. There are several factors that influence energy consumption pattern in breweries such as local climate conditions, production technology, product mix, use of different bottling technologies, capacity utilization [23]. Specific data availability and reliability often limits the estimation of improvement potential and avoids establishing energy efficiency benchmarks adapted to small-to-medium enterprises [21]. Nevertheless, researchers estimated a 40% improvement potential for food and beverage sector [24].

This study was aimed at evaluating the technical and economic feasibility of AD implementation in selected small breweries located in the mountain area of Friuli-Venezia Giulia region (Italy) to improve organic waste and wastewater management, that is currently not efficient, reducing at the same time energy costs. A territory-oriented approach was used, analysing the different organic residues produced in local breweries, as well as the potential methane production in AD processes, both in single digestion and co-digestion. The possibility of installing simple AD reactors at brewery level was investigated. A detailed analysis of the produced organic residues (BSG, BSY, whirlpool residue, end-of-fermentation beer) was made and BMP tests were performed. First-order model and modified Gompertz equation were applied to study AD kinetics. BC and GAC were added to selected BMP tests, to evaluate an eventual increase in methane production. Thermal and electric energy consumptions from a selected brewery were analysed and compared to literature benchmarks. Finally, a simplified AD reactor dimensioning and energy balance were proposed, evaluating the impact of AD plant installation on brewery energy costs.

2. Materials and methods

The samples were collected from local plants, transported to the laboratory and analysed without delay. Inoculum and substrate mixtures for BMP tests were prepared using the desired inoculum-to-substrate (I/S) ratio.

2.1. Inoculum and substrates

Anaerobic sludge was taken from a full-scale anaerobic digester located in Udine wastewater treatment plant (200,000 population equivalent). Commercial GAC (particle size of 50–150 μm) was purchased from Sigma-Aldrich. BC was produced in a downdraft gasifier (Neweng srl, Azzano Decimo) from red spruce woodchips. The 15-kW power plant, operating at 650 °C maximum temperature, was fed with 34 kg/h of raw biomass and yielded about 10% of C-rich BC. Waste samples from two local breweries (BSG, BSY, whirlpool residue, end-of-fermentation beer as for brewery 1; BSG, yeast & hop as for brewery 2) were collected and analysed without delay.

2.2. Analytical methods

Physicochemical characterization was performed according to Standard Methods for Examination of Water and Wastewater [25]. The analysed parameters were: soluble Chemical Oxygen Demand (sCOD), Total Solids (TS), VS, NH_3-N, alkalinity, PO_4^{3-}-P, SO_4^{2-}. For dissolved compounds measure (NH_3-N, alkalinity, PO_4^{3-}-P, SO_4^{2-}) the samples were centrifuged at 10,000 rpm for 10 min before analysis. Soluble COD analysis was carried out after passing the samples through a 0.45 μm cellulose filter. Elemental analysis (C, H, N, S) was executed on dried samples in an elemental analyser (Flash EA1112, ThermoQuest/CE Elantech, Lakewood, NJ); the tests were conducted using automated combustion-reduction at 900 °C, followed by molecular sieve gas chromatography at 60 °C and thermal conductivity detection system [26]. Table 1 summarizes the applied methods for red spruce woodchips and biochar characterization.

2.3. BMP tests

Automatic methane production test system (Bioprocess) was used for BMP tests. The equipment consisted of 15 individually stirred reactors (650 mL volume) inserted in a water bath. Produced biogas was sent to a soda solution that fixed CO_2; the solution contained a pH indicator (tymolphtalein), indicating saturation. The residual biogas (essentially pure methane) was measured in methane registration unit, formed by 15 injection mould flow cells.

I/S ratio was calculated on VS basis and, according to the results of some preliminary tests, a high I/S ratio of 6 was chosen for all tests (except from BSG, where I/S ratio was fixed at 3). I/S was properly set to overcome acid accumulation, NH_3 inhibition or reactor overload. No pH correction or nutrient addition was performed, to properly analyse biomass adaptation to the substrates. Thermostatic bath temperature was set at 35 °C and a discontinuous mixing regime (30 s on-30 s off) was set up. Before starting the tests, each reactor was flushed with N_2 for 30 s, to establish anaerobic conditions [27].

BMP tests were stopped when no CH_4 production was observed for more than 24 h. All the tests were conducted in triplicate with a blank control. Final BMP value was calculated by subtracting blank methane production from sample methane production. For GAC and BC tests, the amount of added carbonaceous material was set at 0.2 g/g $VS_{substrate}$, as suggested in [28]. Co-digestion tests were planned on BSG1 and BSY1 at I/S ratio of 6, and different relative ratios were tested: 70% BSG + 30% BSY, 50% BSG + 50% BSY, 30% BSG + 70% BSY (mass basis). BMP from co-digestion assays was compared to theoretical BMP, calculated from mono-digestion tests.

2.4. Kinetic analysis

General expression of methane evolution using first-order model can be written as in Eq. (1), where G(t) is cumulative CH_4 yield at time t (mL/g VS), G_0 is total methane potential of the substrate (mL/g VS) and k (d^{-1}) is methane production rate constant, assumed as hydrolysis constant [29].

$$G(t) = G_0(1 - e^{-kt}) \tag{1}$$

The first-order model is accurate when hydrolysis is the rate-limiting step and G_0 represents the total yield of hydrolysable VS [30]. Brewery waste is a complex and heterogeneous substrate, rich in lignin compounds, so the approximation of hydrolysis as rate-limiting step appears realistic.

The general expression for modified Gompertz equation was reported in Eq. (2), where R_{max} is the maximum methane production rate (mL/g VS d) and λ represents lag phase duration (d) [14]:

$$G(t) = G_0\exp\left\{-\exp\left[\frac{R_{max}e}{G_0}(\lambda - t) + 1\right]\right\} \tag{2}$$

Eq. (2) was identified as a good empirical non-linear model and was commonly used in literature [14]. Gompertz equation and first-order model were applied to selected BMP tests using a simple regression method. Inferred hydrolysis constant and lag phase duration were obtained; fitting indexes (R^2 and standard deviation) were calculated.

2.5. Energy analysis

Beer production, electricity and natural gas consumption data were given by brewery 1. Natural gas calorific value was assumed as 10.77 kW h/Sm^3 [31]. Thermal consumption was calculated considering a standard boiler efficiency of 0.85. Energy costs were evaluated considering mean Italian electricity (0.20 €/kWh) and gas (0.25 €/Sm^3) costs [32].

Real production of brewery residues was considered, together with BMP yield obtained in the laboratory phase, to estimate CH_4 yield in AD process. Obtainable electric and thermal energy was calculated by considering of burning biogas in a combined heat and power (CHP) unit, having an electric yield of 35% and a thermal yield of 50% [33]. Net energy yields were calculated applying an annual energy balance: net produced thermal energy TE_{net} (kWh/year) was evaluated as difference between thermal production in CHP unit TE_{CHP} (kWh/year), thermal energy required for biomass heating TE_{heat} (kWh/year) and dispersions through digester walls TE_{disp} (kWh/year):

$$TE_{net} = TE_{CHP} - TE_{heat} - TE_{disp} \tag{3}$$

Heat dispersions were calculated following Eq. (4): digester operating temperature T_{dig} was assumed as 35 °C, while biomass initial temperature T_{waste} was taken as 23 °C. Brewery waste specific heat $c_{p,waste}$ was estimated as 4.2 kJ/kg K, while m_{waste} (t/d) represented daily produced waste.

$$TE_{heat} = m_{waste}c_{p,waste}(T_{dig} - T_{waste})\cdot 365\cdot 0.2778 \tag{4}$$

Eq. (5) was used to estimate heat loss through digester walls [34]; A_{disp} (m^2) represents digester surface area, while K is heat flow coefficient, estimated as 2.79 W/h m^{-2} °C^{-1} (concrete walls with 30 mm thickness).

$$TE_{disp} = KA_{disp}(T_{dig} - T_{waste})\cdot 24\cdot 365 \tag{5}$$

Net electricity production EE_{net} (kWh/year) was calculated

Table 1
Applied test methods for biomass and biochar characterization.

Parameter	Test method
Bulk density	DIN 51705
Specific surface area	DIN 66132/ISO 9277
Total water	DIN 51718
Ash	DIN 51719
Gross calorific value	DIN 51900
C, N, H	DIN 51732
O	DIN 51733
pH	DIN ISO 10390

subtracting from electricity production in CHP unit EE_{CHP} (kWh/year) the electricity spent for mixing EE_{mix} (kWh/year), pumping EE_{pump} (kWh/year) and biogas purification EE_{pur} (kWh/year).

$$EE_{net} = EE_{CHP} - EE_{mix} - EE_{pump} - EE_{pur} \tag{6}$$

Mixing energy was calculated following Eq. (7), where h represents mixer working hours (h/year) and f is a utilization factor (fixed at 0.5, coherently with the discontinuous mixing regime used in laboratory tests).

$$EE_{mix} = P_{mix} h \cdot f \tag{7}$$

Mixing power P_{mix} (kW) was evaluated using Eq. (8); digester volume V_{dig} (m^3) was calculated by considering daily production of brewery waste and assuming a retention time at least of 30 days, while mixing intensity G was fixed at 80 s^{-1}. Dynamic viscosity was estimated as $1.14 \cdot 10^{-3}$ Pa s.

$$P_{mix} = G^2 \mu V_{dig} \tag{8}$$

Pumping energy consumption was calculated through Eq. (9), where specific energy consumption for pumping (SE_{pump}) was fixed at 0.1 kW h/m^3 and pump efficiency η was estimated as 75%.

$$EE_{pump} = \frac{SE_{pump} V_{waste}}{\eta} \tag{9}$$

The electricity needed for biogas purification EE_{pur} was estimated, basing on full-plant experiences, as 10% of total electricity production.

$$EE_{pur} = 0.10\, EE_{CHP} \tag{10}$$

3. Results and discussion

The results from physicochemical characterization are reported in Section 3.1, followed by BMP assays results (Sections 3.2–3.5) and energy analysis (Section 3.6).

3.1. Physicochemical characterization

Produced organic waste and wastewater from two local breweries was considered. As for brewery 1 BSG, BSY, whirlpool residue and end-beer were analysed; as for brewery 2 BSG and yeast & hop mixture were studied.

3.1.1. Brewery residues

The results from brewery waste characterization were summarized in Table 2. All the matrices had VS/TS ratio higher than 75% and high soluble COD, indicating good biodegradability and significant CH_4 potential. A mild acidity and a low alkalinity (more pronounced in end-of-fermentation beer) were measured, indicating a possible acidification tendency in BMP tests, if a low I/S ratio should be adopted. Ammonia concentration was well below inhibitory level; phosphate concentration was sufficient to sustain optimum operation of anaerobic bacteria. Sulphates were detected in moderate concentrations.

BSG characterization performed in [3] highlighted a high TS content (in the range of 211–263 g/kg), similar to BSG2 (230.5 g/kg), and a high VS/TS ratio of 96.1% (comparable to BSG1). In [11] TS in BSG was reported as 243.9 g/kg, similar to BSG2; in addition, they measured a high COD concentration of 116.4 g O_2/kg in BSG slurry, after 2.6-fold dilution. As for BSY, in [2] COD concentration of 2.15 g COD/g TS was reported, together with TS of 15.9% (falling in the measured range of 13.47–18.29%) and VS/TS ratio of 92.3%, higher than analysed yeast. As for brewery wastewater, in [3] a neutral pH of 6.8–7.1 was claimed (higher than actual end-beer), TS of 90–280 mg/L (low if compared to end-beer) and Total Nitrogen (TN) concentration of 50–150 mg/L. In [35] TN and Total Phosphorous (TP) concentration in brewery wastewater was reported respectively in the range of 30–100 g N/m^3 and 30–100 g P/m^3; the analysed end-beer had higher phosphate concentration than reported literature range, while NH_3 concentration fell in literature range.

Table 3
Results from elemental analysis of brewery residues.

Substrate	C (%)	H (%)	N (%)	S (%)	C/N
BSG1	47.5	6.5	2.9	< 1	16.4
Whirl 1	45.8	5.6	2.7	< 1	17.0
BSY1	45.6	6.4	8.7	< 1	5.2
End beer 1	43.7	6.3	2.3	< 1	19.0
BSG2	45.6	6.7	2.4	< 1	19.0
BSY & hop 2	49.9	6.0	4.1	< 1	12.2
Sludge	26.4	3.5	3.1	< 1	8.5

Elemental analysis results (Table 3) highlighted a low carbon to nitrogen (C/N) ratio of 5.2 in BSY1 while, given the fact that in brewery 2 BSY was mixed with hop, a higher C/N ratio of 12.2 appeared. BSG, whirlpool residue and end-beer showed a similar C/N ratio (16.4–19.0). A C/N ratio of 20–30 was considered optimum for anaerobic bacterial growth [36] so, from this point of view, the analysed substrates could be successfully digested (except from BSY, where a higher I/S ratio should be adopted). A lower C/N ratio in BSG (3–5), potentially leading to NH_3 inhibition, was highlighted in [3], so they proposed a two-stage AD process to digest this substrate. In [2] it was reported, as for BSG and BSY, C/N ratio respectively of 12.4 (lower than the actual results) and 5.2 (coherent with actual BSY).

3.1.2. Biochar

Red spruce woodchips had high volatile (72%) and low ashes (3%) content; elemental analysis underlined high C (44%) and O (48%) in the raw substrate. The actual yield in BC (10%) was similar to reported literature value for gasification plants [37].

BC characterization results were reported in Table 4; BC produced at high temperature (such as the analysed one) exhibits lower hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratio than that obtained at lower temperature, indicating a gradual increase in aromaticity and decrease in polarity with temperature [38]. Increasing processing temperature increases pH, due to the enrichment of ash content [39], and augments surface area of the final product [40].

In [41] BC characteristics were reported, before adding this material to cow manure AD; the raw material was processed at 500 °C (lower than actual processing temperature) for 4 h. The obtained BC had basic

Table 2
Results from physicochemical characterization of brewery residues.

Substrate	sCOD (g/L)	TS (% w/w)	VS (% w/w)	VS/TS (%)	pH -	Alkalinity (mg $CaCO_3$/L)	NH_3-N(mg N/L)	PO_4^{3-}P (mg P/L)	SO_4^{2-} (mg/L)
BSG1	41.5	15.99	15.53	97.15	5.8	298	78	280	15.1
Whirl 1	111.0	12.93	10.72	82.86	5.8	470	625	410	59.7
BSY1	n.d.	18.29	13.96	76.35	6.1	905	160	n.d.	65.3
End beer 1	26.0	3.77	3.56	94.47	5.2	322	65	200	180
BSG2	n.d.	23.05	18.12	78.62	5.8	n.d.	n.d.	n.d.	n.d.
BSY & hop 2	133.8	13.47	11.47	85.19	5.2	282	417	820	42.3
Sludge	0.97	4.86	2.31	47.50	7.2	1647	265	343	< 2

Table 4
Results from biochar characterization.

Parameter	Value
Bulk density (kg/m^3)	446
Specific surface area (m^2/g)	327
Total water (% w/w)	2.6
Ash content (% w/w)	6.1
Gross calorific value (kJ/kg)	30,875
H (% w/w)	1.54
C (% w/w)	87.7
N (% w/w)	0.41
H/C	0.21
O/C	0.01
pH	8.4

pH of 8.5 (similar to the actual BC), a lower surface area of 112.6 m^2/g and a significantly lower C concentration of 16.9%.

3.2. BMP mono-digestion tests

Meaningful input parameters to BMP tests, including I/S ratio, TS, VS, inoculum and substrate mass were reported in Table 5. In the tests with the addition of carbonaceous material (BC and GAC), the same amounts of inoculum and substrate were used as in mono-digestion tests.

The results from mono-digestion BMP tests were depicted in Fig. 1. The high methane potential of BSY1 (up to 486.9 N L CH_4/kg VS_{added}) emerged, while BSG from the two breweries gave a similar methane production of 306.4–356.2 NL CH_4/kg VS_{added}. Whirlpool residue produced a slightly lower BMP value of 290.3 N L CH_4/kg VS_{added} and was digested with a slower kinetics, if compared to BSG1. Interestingly, the lowest methane productions were obtained from end-beer 1 (126.0 N L CH_4/kg VS_{added}) and BSY&hop 2 (31.9 N L CH_4/kg VS_{added}).

The low BMP yield from end-beer could be explained with the occurrence of acidification phenomenon: methane production was very intense in the first digestion day, but suddenly stopped in the successive period due to high VFA generation, that reduced pH to 5.0. Low BMP from BSY&hop mixture, instead, was due to the significant presence of lignin and recalcitrant compounds in the mixture, not easily biodegradable. The obtained results could be related also to the availability of nutrients (N and P): in [42] it was demonstrated that an increase in N and P in the raw substrate stimulates the production of higher concentration of VFA in the acidogenic phase, and also the methanogenic phase is consequently stimulated. However, an augment in N leads to a reduction of CH_4 percentage in biogas, while P increase, on the other hand, increases also CH_4 content in biogas. The high methane production from BSY could be thus related to its high N and P concentration, as pointed out in Table 2, while, on the other hand, the low CH_4 production from end-beer could be somehow linked with its low concentration in nutrients.

BSG mono-digestion was tested in [11]: a BMP value of 285 N L CH_4/kg VS_{added} was reported, lower than the obtained results. In [3], BMP value from BSG was claimed to be 187–273 L CH_4/kg VS_{added}, again lower than actual BMP. The better results in this study could be explained with a more favourable C/N ratio of the matrices and a higher water content, that allowed a faster hydrolysis phase. Higher CH_4 production than the obtained one was claimed in [43], where a yield of 0.75-1.12 m^3 gas/kg TS was reported (CH_4 content of 55–70%); the highest production in the present work from BSY1 was 0.487 m^3 CH_4/kg VS (0.372 m^3 CH_4/kg TS). High COD removal efficiency (78–98%) was underlined from AD of brewery wastewater in [43], together with biogas yield up to 0.53 L/g $COD_{removed}$ (0.224 L CH_4/g COD_{added}), higher than actual end-beer (0.126 N L CH_4/g VS, correspondent to 0.173 N L CH_4/g COD_{added}).

In [2] maximum theoretical methane yield from BSG and BSY were reported to be respectively 0.408 L CH_4/g VS and 0.350 L CH_4/g COD (0.815 L CH_4/g VS), calculated from Buswell equation application. If the same value was assumed also for the analysed substrates (that come from comparable scale breweries in the same geographic area), it could be seen that BSG gave a CH_4 yield as high as 75.1–87.3% of the theoretical value, while BSY produced only 59.7% of the theoretical yield; it appeared evident that an unexploited CH_4 potential was present in BSY.

3.3. Kinetic analysis

The results from kinetic analysis were summarized in Table 6. The analysed BSG was digested with an inferred hydrolysis constant k of 0.23-0.33 d^{-1}, higher than reported literature value for cellulose (0.15 d^{-1}) [44], while BSY and whirlpool residue were digested with a higher k of 0.35-0.36 d^{-1}. Lag phase duration λ was generally short for all selected substrates, except from whirlpool residue, where a longer λ (5.9 d) was observed. This was visible also from BMP curves (Fig. 1), which highlighted a slow methane production from this matrix, due to a general low biodegradability. A good correlation between predicted and measured methane yields was underlined both from R^2, that was always higher than 0.97, and standard deviation, that was lower than 10%, except from Gompertz model application on whirlpool residue.

In [45] modified Gompertz equation was applied to co-digestion of cattle manure and BSG. A reduction in lag phase duration from 1.52 to 0.78 d with increasing BSG fraction (from 0% to 30%) was observed; methane production increased from 11.14 to 19.72 L, indicating good complementary characteristics of the substrates. In [46], the digestion characteristics of cellulose, hemicellulose and lignin were presented; measured methane yield from these molecules was in the range of 178.6–251.4 mL CH_4/g VS. Gompertz equation application showed that lignin compounds produced a long lag-phase duration, from 3.0 days up to 18.1 days [46], so the longer λ, observed in whirlpool residue, could be explained with a significant lignin concentration.

3.4. Effect of GAC and BC on BMP yield

The effect of GAC and BC addition on BMP curves was summarized in Figs. 2–4. A substantial increase in BMP value was observed on BSY, both with the addition of GAC (642.2 N L CH_4/kg VS_{added}) and BC (641.0 N L CH_4/kg VS_{added}). Whirlpool residue gave a higher BMP only when adding biochar (404.4 N L CH_4/kg VS_{added}), while granular carbon addition did not improve final methane yield. Conflicting effects appeared on BSG: a significant increase in BMP, up to 388 N L CH_4/kg VS_{added} (+26.6%), was observed in BSG2, while even a reduction in final BMP (341.8 N L CH_4/kg VS_{added}) was encountered in BSG1. Biochar addition to end-beer produced again acidification, with a low final CH_4 yield (151 N L CH_4/kg VS_{added}).

The significant increase in BMP yield observed on brewery residues could be explained, in the case of BSY, with the low C/N ratio of the substrate: for this particular substrate, the addition of carbon-rich additives dramatically improved the operating conditions for anaerobic

Table 5
Input parameters for BMP tests.

Test	I/S ratio	VS (% w/w)	TS (% w/w)	Mass inoculum (g)	Mass substrate (g)
BSG1	3	15.91	15.99	381.6	18.4
BSY1	6	13.96	18.29	389.3	10.7
Whirlpool 1	6	10.72	12.93	386.2	13.8
End beer 1	6	3.56	3.77	361.0	39.0
BSG2	3	18.12	23.05	383.7	16.3
BSY hop 2	6	11.47	13.47	387.0	13.0
70% BSG1 + 30% BSY1	6	15.33	16.68	390.2	9.8
50% BSG1 + 50% BSY1	6	14.94	17.14	390.0	10.0
30% BSG1 + 70% BSY1	6	14.55	17.60	389.7	10.3

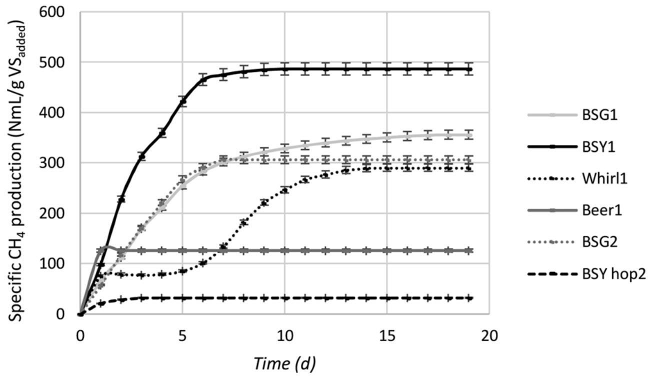

Fig. 1. BMP mono-digestion tests results.

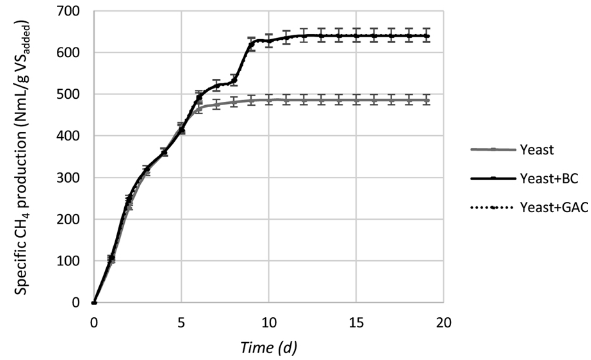

Fig. 2. Effect of BC and GAC addition in BMP curves of BSY.

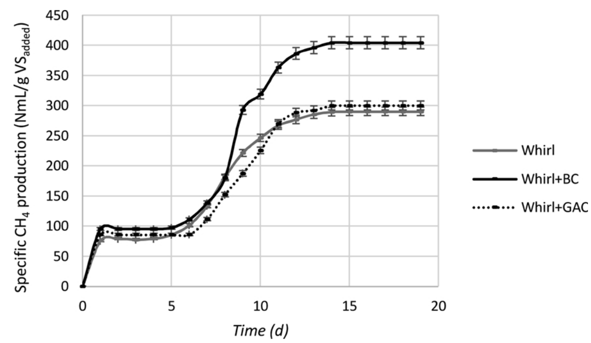

Fig. 3. Effect of BC and GAC addition in BMP curves of whirlpool residue.

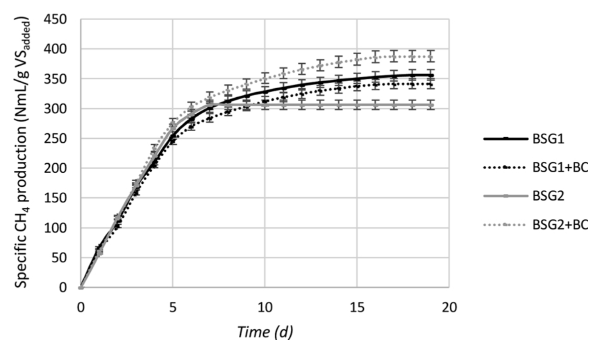

Fig. 4. Effect of BC addition in BMP curves of BSG.

bacteria. In literature it was shown that the addition of charcoal or activated carbon to AD of N-rich substrates (such as cattle dung or swine manure) stimulated an increase in biogas yield [47]; N-rich substrates are very attractive feedstocks for biogas production [18], given the high methane yield obtainable from protein degradation. In the case of whirlpool residue, where only biochar addition increased methane yield, the effect could be ascribed to peculiar biochar characteristics (such as porous morphology and surface crevices) that provided better conditions for microorganism adhesion [48], while granular activated carbon did not produce any significant variation in microbial activity. This conflicting outcome could be due also to the high concentration of lignin in whirlpool residue, not easily biodegradable, and the extreme heterogeneity of whirlpool residue. Similar considerations could be made also for the conflicting results obtained on BSG, having similar characteristics to whirlpool residue.

Different kinds of BC were added to AD of citrus peel waste in [49]: they claimed that wood BC (similar to actual BC) produced the shortest lag phase, while coconut shell BC gave the highest methane yield. In [50] it was reported that the addition of 10 g/L of BC (higher than the actual dosage of 0.2 g/g $VS_{substrate}$) to dairy manure increased methane yield in the range of 24.7–35.7%. Furthermore, a shorter lag phase duration was highlighted, together with lower volatile fatty acids concentration. In [20], BC addition to AD of simulated food waste shortened lag phase duration of 41–45%, increasing maximum production rate by 23.0–41.6% and BMP value by 1.9–9.6%. In [51] the effect of BC addition on different substrates was studied, including chicken manure, characterized by high TS content of 27.92% w/w (similar to BSG2) and low C/N ratio of 9.22; a significant increase in CH_4 production (up to +69%) was obtained.

BC addition in the present study had a strong effect in increasing methane yield in particular on BSY, and a synergism between advanced thermal processes (producing biochar) and anaerobic digestion should be encouraged, contributing to circular economy perspective. BC stimulates direct interspecies electron transfer between bacteria and methanogenic archaea in AD, accelerating the conversion of organic compounds to CH_4 [52]. In addition, the positive effect of BC is related to bacteria colonization of the high surface area, that shortens the lag time required for methane formation, as well as enhancing acids production and degradation [51]. Methanogenic archaea (such as *Methanosarcina*) were shown to reside deep within the core channels of BC: the high surface area of the material aided in establishing methanogenic zones, enhancing methane yield [53]. The integration of thermochemical processes with AD represents an interesting strategic approach towards a sustainable resource conversion and management [54], able to expand the range of available feedstocks to biologically recalcitrant substrates (such as woody materials), leading to the development of sustainable circular economies [55].

3.5. BMP co-digestion tests

Co-digestion tests were planned on BSG and BSY. The results (Fig. 5) did not underline a substantial increase in BMP yield, if compared to

Table 6
Results from kinetic analysis on selected BMP tests.

Substrate	R_{max} (mL/g VS d)	λ (d)	R^2 Gompertz	Std dev Gompertz (%)	k (d^{-1})	R^2 first-order	Std dev first order (%)
BSG1	66.6	0.6	0.9905	6.3	0.23	0.9956	2.2
Whirl1	75.7	5.9	0.9704	16.7	0.36	0.9887	2.6
BSY1	130.0	0.4	0.9931	3.6	0.35	0.9892	3.1
BSG2	60.5	0	0.9948	1.1	0.33	0.9780	3.7

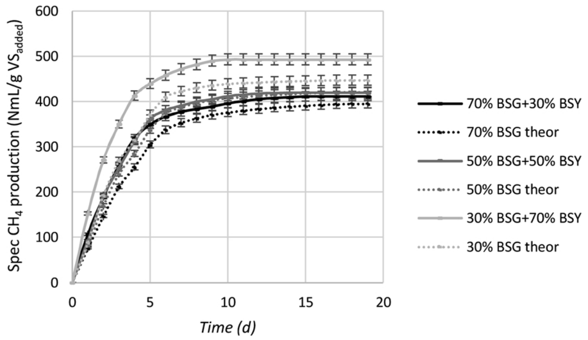

Fig. 5. Results from co-digestion tests (BSG + BSY).

single digestion tests. The increase in final BMP, compared to theoretical methane production of the mixture (calculated using single digestion curves, reported in Section 3.2), was in the range of 5–10%. However, a significantly faster kinetics (up to +40% after 2 days) was observed in co-digestion tests, highlighting a positive co-digestion effect.

In [56] it was reported that the addition of glucose or acetate (readily biodegradable substrates) to BSG, that is rich in lignin, significantly enhanced CH_4 yield (+35%, from 381 to 516 mL biogas/g $COD_{removed}$). In [7] a good methane yield (up to 0.30 L CH_4/g VS_{added}) was reported when co-digesting cow manure and brewery waste, due to the complementary characteristics of the substrates.

The faster methane production kinetics obtained in this study could be explained with a more balanced C/N ratio of the mixture, compared to single BSY digestion; in addition, spent yeast is expected to work simultaneously with anaerobic bacteria, augmenting methane production from BSG and accelerating hydrolysis phase. As visible from Fig. 5, given the higher methane yield from BSY (if compared to BSG), an increase in BSY percentage in the mixture consequently leads to an increase in total methane yield. A remarkable work [57] studied co-digestion of BSY and brewery wastewater in a UASB reactor: stable operations and high COD removal (mean 92.4%) were claimed, highlighting the substantial biodegradability of the mixture. Moreover, it was shown that yeast pre-treatment did not increase obtainable methane yield, being already easily biodegradable.

3.6. Energy analysis

In brewery 1 produced beer was in the range of 2,940–4,628 h L/year, specific electricity (EE) consumption was 130.6–148.9 MJ/hL and thermal energy (TE) need was 116.4–147.0 MJ/hL. Total energy costs were estimated around 25,000 €/year for the years 2016 and 2017 while, due to an increase in produced beer in 2018, this cost was expected to arise up to 42,866 €/year (estimation based on the first 7 months of 2018).

In [21] it was reported from a Latvian brewery (producing 15,000–17,000 h L beer/year, larger than analysed brewery) a specific EE consumption of 81.2–92.2 MJ/hL (lower than actual brewery), while a significantly higher TE consumption of 219.2–231.3 MJ/hL was claimed. BSG, similarly to what is done also in the analysed breweries, was supplied to farmers as animal feed. In [58] it was reported for a micro-brewery located in Northeast England an electricity consumption of 320 kW h/d and a thermal consumption of 2816 kW h/d, while in the analysed brewery a similar daily electricity consumption of 310–321 kW h/d and a lower thermal consumption of 185–336 kW h/d arose.

In Table 7 total produced mass of organic wastes in brewery 1 was reported, together with BMP yield obtained in Sections 3.3–3.4, to estimate electric and thermal energy that could be produced implementing a simple AD reactor at brewery level. For all the substrates, the maximum BMP (obtained adding BC to the reactors) was considered, hypothesizing a synergism with local biomass plants, that could furnish BC. From Table 7 it could be seen that BSG was the main organic residue (87%, VS mass basis), BSY accounted for 10.4%, while whirlpool and end-beer contributed for the residual 2.6%.

AD reactor implementation at brewery level could lead to significant energy costs reduction for the analysed plant: biogas, if burned in a conventional CHP unit, could provide up to 69,821 kW h_{el}/year of electricity and 99,744 kWh_{ter}/year of heat. In Fig. 6 a simplified plant scheme for the analysed brewery was reported, highlighting input and outputs to the system, as well as connections between AD plant and brewery. The applied energy balance (Table 8) on a digester having a volume of 65 m^3 (corresponding to a mean retention time of 31.6 d) showed that the main thermal losses were dispersions through digester walls, while electricity needs for mixing and pumping were negligible. Net electricity production from AD reactor corresponded to 53.9% of the total plant need, while net heat production was 64.4% of the total thermal request. Operating parameters, as for the installed AD plant, would be the following: HRT was set at 31.6 d, while OLR was calculated as 2.31 kg VS/m^3d (equal to Volumetric Loading Rate, VLR). VS and TS of the mixture would be respectively 14.81% and 15.73%.

BC cost was evaluated considering a dosage of 0.2 g/g VS for BSY and whirlpool, as done in the laboratory tests: yearly, 1.1 t of BC would be needed. Considering a mean Italian BC cost of 5 €/kg, the cost for BC purchase would be about 5400 €/year. The availability of local incentives for CO_2 emissions reduction, such as white certificates and incentive tariff, would allow to cover this extra expense for the analysed brewery, confirming the sustainability of the process. The process scalability to larger scale breweries depends on the local availability of low-cost biomass, amenable to be transformed to BC; larger breweries, however, can typically sustain a higher investment cost, installing higher efficiency systems for biogas conversion (such as biogas upgrading to biomethane), so payback time could be reduced, in comparison with little breweries.

The sustainability of AD implementation in small breweries was confirmed also in [58], where an increase in overall system efficiency of 10% appeared when using biogas in CHP units, instead of diesel fuel. Furthermore, they highlighted that biogas has effect of net zero carbon emissions, enhancing the enterprise sustainability. The installation of simple digesters, characterized by an easy of operations, should be privileged in rural and mountain areas (such as the analysed one), because of the little scale of the plants. In literature the installation of tubular digesters was recommended, due to simple design and construction [59]. In [60] a full-scale tubular digester treating cattle manure was monitored and stable operations were reported, together with good digestate agricultural impact. This approach could be applied also to local breweries, where digestate could be used as precursor for BC production.

4. Conclusions

Brewery residues investigation for anaerobic digestion implementation at plant level was carried out. BMP tests highlighted a good biodegradability of the analysed residues, in particular spent yeast and spent grain. The addition of granular activated carbon and biochar significantly increased methane yields from brewery residues, in

Table 7
Obtainable CH_4 yield from selected substrates in brewery 1.

Substrate	Mass (kg VS/year)	BMP (NL CH_4/kg VS_{added})	CH_4 yield (Nm^3/year)
BSG	41,939	356	14,930
BSY	5,027	641	3,222
Whirlpool	756	404	305
Beer	428	151	65
Total	**48,150**	–	**18,522**

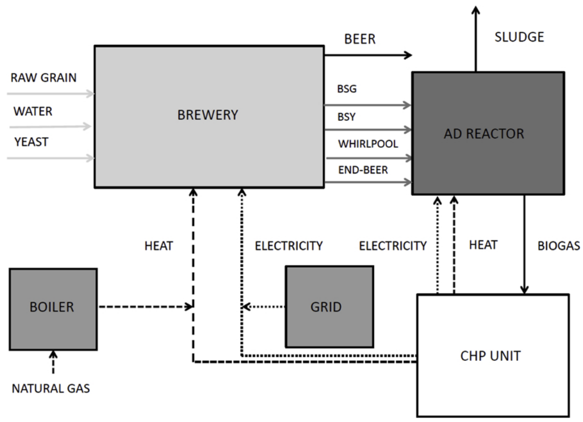

Fig. 6. Simplified plant scheme after AD implementation.

Table 8
Thermal and electric energy analysis.

Thermal energy (kWh/year)				Electric energy (kWh/year)				
TE_{CHP}	TE_{heat}	TE_{disp}	TE_{net}	EE_{CHP}	EE_{mix}	EE_{pump}	EE_{pur}	EE_{net}
99,744	5,191	18,768	75,785	69,821	1,826	88	6,982	60,925

particular spent yeast, underlining a positive connection between thermal processes and anaerobic digestion. Reduction in transport and management costs of the produced waste could be successfully achieved, together with a positive move towards circular economy. Co-digestion tests revealed a moderate synergism between spent grain and spent yeast, given the complementary characteristics of the substrates, in particular regarding C/N ratio. A simple kinetic analysis was applied, underlining the difference in reaction rates between the analysed substrates. An energy analysis on a local brewery revealed that anaerobic digestion implementation at brewery level, through a 65 m^3 reactor, is sustainable and can provide most of the energy need of the plant, reducing the pay-back time for the investment.

Declaration of interests

None.

This research did not receive any specific grant from funding agencies in the public, commercial, or non-for-profit sectors.

Acknowledgements

The authors acknowledge local breweries (Zahre brewery- Sauris and Garlatti-Costa brewery- Forgaria) for the active collaboration in the research work.

References

[1] L. Fillaudeau, P. Blanpain-Avet, G. Daufin, Water, wastewater and waste management in brewing industries, J. Clean. Prod. 14 (2006) 463–471, https://doi.org/10.1016/j.jclepro.2005.01.002.

[2] R. Vitanza, A. Cortesi, V. Gallo, I. Colussi, M.E. De Arana-Sarabia, Biovalorization of brewery waste by applying anaerobic digestion, Chem. Biochem. Eng. Q. 30 (3) (2016) 351–357, https://doi.org/10.15255/CABEQ.2015.2237.

[3] M. Panjičko, G.D. Zupančič, L. Fanedl, R.M. Logar, M. Tisma, B. Zelic, Biogas production from brewery spent grain as a mono-substrate in a two-stage process composed of solid-state anaerobic digestion and granular biomass reactors, J. Clean. Prod. 166 (2017) 519–529, https://doi.org/10.1016/j.jclepro.2017.07.197.

[4] M.I. Baloch, J.C. Akunna, P.J. Collier, The performance of a phase separated granular bed bioreactor treating brewery wastewater, Bioresour. Technol. 98 (9) (2007) 1849–1855, https://doi.org/10.1016/j.biortech.2006.06.014.

[5] G.D. Zupančič, I. Skrjanec, R. Marinsek Logar, Anaerobic co-digestion of excess brewery yeast in a granular biomass reactor to enhance the production of biomethane, Bioresour. Technol. 124 (2012) 328–337, https://doi.org/10.1016/j.biortech.2012.08.064.

[6] G.D. Zupančič, M. Ros, M. Klemencic, M. Oset, R. Marinsek-Logar, Biogas production from brewery yeast in an EGSB reactor, Brauwelt Intl. 34 (2016) 108–113.

[7] M.N.I. Siddique, Z.A. Wahid, Achievements and perspectives of anaerobic co-digestion: a review, J. Clean. Prod. 14 (2018) 359–371, https://doi.org/10.1016/j.jclepro.2018.05.155.

[8] C.A. Henard, H.K. Smith, M.T. Guarnieri, Phosphoketolase overexpression increases biomass and lipid yield from methane in an obligate methanotrophic biocatalyst, Metab. Eng. 41 (2017) 152–158, https://doi.org/10.1016/j.ymben.2017.03.007.

[9] G.D. Zupančič, M. Klemenčič, M. Stražiščar, Improving the energy balance in brewing industry using waste yeast as an energy substrate, in: A.G. Olabi (Ed.), Sustainable Energy Beyond 2020. Proceedings of the 3rd International Conference on Sustainable Energy & Environmental Protection: Part 2 (2009) 64–69.

[10] S.I. Mussatto, Brewer's spent grain: a valuable feedstock for industrial applications, J. Sci. Food Agric. 94 (2013) 1264–1275, https://doi.org/10.1002/jsfa.6486.

[11] C. Bougrier, D. Dognin, C. Laroche, V. Gonzalez, D. Benali-Raclot, J.A.C. Rivero, Anaerobic digestion of brewery spent grains: trace elements addition requirement, Bioresour. Technol. 247 (2018) 1193–1196, https://doi.org/10.1016/j.biortech.2017.08.211.

[12] B. Weber, E.A. Stadlbauer, Sustainable paths for managing solid and liquid waste from distilleries and breweries, J. Clean. Prod. 149 (2017) (2017) 38–48, https://doi.org/10.1016/j.jclepro.2017.02.054.

[13] L.F. Pearse, J.P. Hettiaratchi, S. Kumar, Towards developing a representative biochemical methane potential (BMP) assay for landfilled municipal solid waste – a review, Bioresour. Technol. 254 (2018) 312–324, https://doi.org/10.1016/j.biortech.2018.01.069.

[14] G.K. Kafle, L. Chen, Comparison on batch anaerobic digestion of five different livestock manures and prediction of biochemical methane potential (BMP) using different statistical models, Waste Manage. 48 (2016) 492–502, https://doi.org/10.1016/j.wasman.2015.10.021.

[15] G.D. Gioannis, A. Muntoni, G. Cappai, S. Milia, Landfill gas generation after mechanical biological treatment of municipal solid waste: estimation of gas generation rate constants, Waste Manage 29 (3) (2009) 1026–1034, https://doi.org/10.1016/j.wasman.2008.08.016.

[16] Z.Z. Ismail, A.R. Talib, Recycled medical cotton industry waste as a source of biogas recovery, J. Clean. Prod. 112 (5) (2016) 4413–4418, https://doi.org/10.1016/j.jclepro.2015.06.069.

[17] M.O. Fagbohungbe, B.M.J. Herbert, L. Hurst, C.N. Ibeto, H. Li, S.Q. Usmani, K.T. Semple, The challenges of anaerobic digestion and the role of biochar in optimizing anaerobic digestion, Waste Manage. 61 (2017) 236–249, https://doi.org/10.1016/j.wasman.2016.11.028.

[18] J. Mumme, F. Srocke, K. Heeg, M. Werner, Use of biochars in anaerobic digestion, Bioresour. Technol. 164 (2014) 189–197, https://doi.org/10.1016/j.biortech.2014.05.008.

[19] Y. Yang, Y. Zhang, Z. Li, Z. Zhao, X. Quan, Z. Zhao, Adding granular activated carbon into anaerobic sludge digestion to promote methane production and sludge decomposition, J. Clean. Prod. 149 (2017) 1101–1108, https://doi.org/10.1016/j.jclepro.2017.02.156.

[20] N.M. Sunyoto, M. Zhu, Z. Zhang, D. Zhang, Effect of biochar addition on hydrogen and methane production in two-phase anaerobic digestion of aqueous carbohydrates food waste, Bioresour. Technol. 219 (2016) 29–36, https://doi.org/10.1016/j.biortech.2016.07.089.

[21] A. Kubule, L. Zogla, J. Ikaunieks, M. Rosa, Highlights on energy efficiency improvements: a case of a small brewery, J. Clean. Prod. 138 (2016) 275–286, https://doi.org/10.1016/j.jclepro.2016.02.131.

[22] A. Trianni, E. Cagno, E. Worrell, G. Pugliese, Empirical investigation of energy efficiency barriers in Italian manufacturing SMEs, Energy 49 (2013) 444–458, https://doi.org/10.1016/j.energy.2012.10.012.

[23] L. Zogla, G. Zogla, A. Beloborodko, M. Rosa, Process benchmark for evaluation energy performance in breweries, Energy Procedia 72 (2015) 202–208, https://doi.org/10.1016/j.egypro.2015.06.029.

[24] D. Saygin, E. Worrell, M.K. Patel, D.J. Gielen, Benchmarking the energy use of energy-intensive industries in industrialized and in developing countries, Energy 36 (2) (2011) 6661–6673, https://doi.org/10.1016/j.energy.2011.08.025.

[25] APHA, Standard methods for the examination of water and wastewater, American Public Health Association, 22nd ed., America Water Works Association, Water Environment Federation, Washington DC, 2012.

[26] M. Mainardis, V. Cabbai, G. Zannier, D. Visintini, D. Goi, Characterization and BMP tests of liquid substrates for high-rate anaerobic digestion, Chem. Biochem. Eng. Q. 31 (4) (2017) 509–518, https://doi.org/10.15255/CABEQ.2017.1083.

[27] K. Koch, Y.B. Fernandez, J.E. Drewes, Influence of headspace flushing on methane production in Biochemical Methane Potential (BMP) tests, Bioresour. Technol. 186 (2015) 173–178, https://doi.org/10.1016/j.biortech.2015.03.071.

[28] J.H. Ko, N. Wang, T. Yuan, F. Lu, P. He, Q. Xu, Effect of nickel-containing activated carbon on food waste anaerobic digestion, Bioresour. Technol. 266 (2018) 516–523, https://doi.org/10.1016/j.biortech.2018.07.015.

[29] G.K. Kafle, S.H. Kim, Anaerobic treatment of apple waste with swine manure for biogas production: batch and continuous operation, Appl. Energy 103 (2013) 61–72, https://doi.org/10.1016/j.apenergy.2012.10.018.

[30] P. Parameswaran, B.E. Rittmann, Feasibility of anaerobic co-digestion of pig waste and paper sludge, Bioresour. Technol. 124 (2012) 163–168, https://doi.org/10.1016/j.biortech.2012.07.116.

[31] SNAM, http://www.snam.it/it/trasporto/Archivio/Anno-termico_2016_2017/, 2016 (Accessed 04 November 2018).

[32] ARERA, Italian Authority for Energy, Grids and Environment [Autorità di Regolazione per Energia, Reti e Ambiente], (2018) (accessed 10 October 2018),

https://www.arera.it.
[33] Cogengreen S.A., http://www.cogengreen.com/en/75-402-kw-natural-gas-fired-ecogen-chpunits-natural-gas-fired-condensing-micro-and-mini-chp-units, 2018 (accessed 07 November 2018).
[34] J.R. Banu, S. Sugitha, R.Y. Kannah, S. Kavitha, I.T. Yeom, Marsilea spp.-a novel source of lignocellulosic biomass: effect of solubilized lignin on anaerobic biodegradability and cost of energy products, Bioresour. Technol. 255 (2018) 220–228, https://doi.org/10.1016/j.biortech.2018.01.103.
[35] A.A. Olajire, The brewing industry and environmental challenges, J. Clean. Prod. (2012), https://doi.org/10.1016/j.jclepro.2012.03.003.
[36] R. Xu, K. Zhang, P. Liu, A. Khan, J. Xiong, F. Tian, X. Li, A critical review on the interaction of substrate nutrient balance and microbial community structure and function in anaerobic co-digestion, Bioresour. Technol. 247 (2018) 1119–1127, https://doi.org/10.1016/j.biortech.2017.09.095.
[37] M. Inyang, E. Dickenson, The potential role of biochar in the removal of organic and microbial contaminants from potable and reuse water: review, Chemosphere 134 (2015) 232–240, https://doi.org/10.1016/j.chemosphere.2015.03.072.
[38] W. Suliman, J.B. Harsh, N.I. Abu-Lail, A.M. Fortuna, I. Dallmeyer, M. Garcia-Perez, Influence of feedstock source and pyrolysis temperature on biochar bulk and surface properties, Biomass Bioenergy 84 (2016) 37–48, https://doi.org/10.1016/j.biombioe.2015.11.010.
[39] S. Gul, J.K. Whalen, B.W. Thomas, V. Sachdeva, H. Deng, Physico-chemical properties and microbial responses in biochar-amended soils: mechanisms and future directions, Agric., Ecosyst. Environ. 206 (2015) 46–59, https://doi.org/10.1016/j.agee.2015.03.015.
[40] M. Keiluweit, P.S. Nico, M.G. Johnson, M. Kleber, Dynamic molecular structure of plant biomass-derived black carbon (biochar), Environ. Sci. Technol. 44 (2010) 1247–1253, https://doi.org/10.1021/es9031419.
[41] C. Sun, Z. Song, J. Wang, Y. Li, Y. Pan, T. Sheng, L. Li, Feasibility of dry anaerobic digestion of beer lees for methane production and biochar enhanced performance at mesophilic and thermophilic temperature, Bioresour. Technol. 276 (2019) 65–73, https://doi.org/10.1016/j.biortech.2018.12.105.
[42] P. Boonsawang, A. Rergnarong, C. Tongurai, S. Chaiprapat, Effect of nitrogen and phosphorous on the performance of acidogenic and methanogenic reactors for treatment of biodiesel wastewater, Songklanakarin J. Sci. Technol. 36 (6) (2014) 643–649.
[43] M.K. Arantes, H.J. Alves, R. Sequinel, E.A. da Silva, Treatment of brewery wastewater and its use for biological production of methane and hydrogen, Int. J. Hydrogen Energy 42 (42) (2017) 26243–26256, https://doi.org/10.1016/j.ijhydene.2017.08.206.
[44] IWA Task Group for Mathematical Modelling of Anaerobic Digestion Processes, Anaerobic Digestion Model No. 1 (ADM1). Scientific and Technical Report No. 13, IWA Publishing, London, 2002.
[45] L.S. Mallmann, M.A. Zambom, D.G.T. Batista, L.C. Souza, J.L.G. Silva, S.R.M. Coelho, S.D. Gomes, Potential methane production from manure of cattle fed diet supplemented with wet brewery grain, J. Food Agric. Environ. 12 (2014) 203–208.
[46] W. Li, H. Khalid, Z. Zhu, R. Zhang, G. Liu, C. Chen, E. Thorin, Methane production through anaerobic digestion: participation and digestion characteristics of cellulose, hemicellulose and lignin, Appl. Energy 226 (2018) 1219–1228, https://doi.org/10.1016/j.apenergy.2018.05.055.
[47] M. Desai, D. Madamwar, Anaerobic digestion of a mixture of cheese whey, poultry waste and cattle dung: a study of the use of adsorbents to improve digester performance, Environ. Pollut. 86 (3) (1994) 337–340, https://doi.org/10.1016/0269-7491(94)90174-0.
[48] M. Morita, K. Sasaki, Factors influencing the degradation of garbage in methanogenic bioreactors and impacts on biogas formation, Appl. Microbiol. Biotechnol. 94 (2012) 575–582, https://doi.org/10.1007/s00253-012-3953-z.
[49] M.O. Fagbohungbe, B.M.J. Herbert, L. Hurst, H. Li, S.Q. Usmani, K.T. Semple, Impact of biochar on the anaerobic digestion of citrus peel waste, Bioresour. Technol. 216 (2016) 142–149, https://doi.org/10.1016/j.biortech.2016.04.106.
[50] H.M. Jang, Y.K. Choi, E. Kan, Effects of dairy manure-derived biochar on psychrophilic, mesophilic and thermophilic anaerobic digestions of dairy manure, Bioresour. Technol. 250 (2018) 927–931, https://doi.org/10.1016/j.biortech.2017.11.074.
[51] J. Pan, J. Ma, X. Liu, L. Zhai, X. Ouyang, H. Liu, Effects of different types of biochar on the anaerobic digestion of chicken manure, Bioresour. Technol. 275 (2019) 258–265, https://doi.org/10.1016/j.biortech.2018.12.068.
[52] S. Barua, B.R. Dhar, Advances towards understanding and engineering direct interspecies electron transfer in anaerobic digestion, Bioresour. Technol. 244 (2017) 698–707, https://doi.org/10.1016/j.biortech.2017.08.023.
[53] C.H. Luo, F. Lu, L.M. Shao, P.J. He, Application of eco-compatible biochar in anaerobic digestion to relieve acid stress and promote the selective colonization of functional microbes, Water Res. 68 (2015) 710–718, https://doi.org/10.1016/j.watres.2014.10.052.
[54] S.A. Opatokun, V. Strezov, T. Kan, Product based evaluation of pyrolysis of food waste and its digestate, Energy 92 (3) (2015) 349–354, https://doi.org/10.1016/j.energy.2015.02.098.
[55] F.B. Luz, S. Cordiner, A. Manni, V. Mulone, V. Rocco, R. Braglia, A. Canini, Ampelodesmos mauritanicus pyrolysis biochar in anaerobic digestion process: evaluation of the biogas yield, Energy 161 (2018) 663–669, https://doi.org/10.1016/j.energy.2018.07.196.
[56] I.C. Goncalves, A. Fonseca, A.M. Morao, H.M. Pinheiro, A.P. Duarte, M.I.A. Ferra, Evaluation of anaerobic co-digestion of spent brewery grains and an azo dye, Renew. Energy 74 (2015) 489–496, https://doi.org/10.1016/j.jclepro.2017.09.089 https://doi.org/10.1016/j.renene.2014.08.053.
[57] K. Neira, D. Jeison, Anaerobic co-digestion of surplus yeast and wastewater to increase energy recovery in breweries, Water Sci. Technol. 61 (5) (2010) 1129–1135, https://doi.org/10.2166/wst.2010.052.
[58] B. Sturm, M. Butcher, Y. Wang, Y. Huang, T. Roskilly, The feasibility of the sustainable energy supply from bio wastes for a small scale brewery- a case study, Appl. Therm. Eng. 39 (2012) 45–52, https://doi.org/10.1016/j.applthermaleng.2012.01.036.
[59] M. Kinyua, L. Rowse, S. Ergas, Review of small-scale tubular anaerobic digesters treating livestock waste in the developing world, Renew. Sustain. Energy Rev. 58 (2016) 896–910, https://doi.org/10.1016/j.rser.2015.12.324.
[60] L. Castro, H. Escalante, J. Jaimes-Estevez, L.J. Diaz, K. Vecino, G. Rojas, L. Mantilla, Low cost digester monitoring under realistic conditions: rural use of biogas and digestate quality, Bioresour. Technol. 239 (2017) 311–317, https://doi.org/10.1016/j.biortech.2017.05.035.